Electrochromic Properties of Tungsten Oxides Synthesized from Aqueous Solutions

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Abstract. Tungsten oxides are known to exhibit interesting electrochemical properties. Ion insertion (Li^+, H^+) within the oxide network is highly reversible. It leads to a blue coloration and WO_3 thin films can be used as electrochromic layers in display devices or smart windows.

Tungsten oxide thin films can be conveniently deposited from aqueous solutions of tungstic acid. However polytungstic acids are not stable and tend to precipitate into hydrated tungsten oxide $WO_3 \cdot 2H_2O$. The condensation of polytungstic species can be chemically controlled by adding foreign ions in the solution. Precipitation is no more observed in the presence of H_2O_2. Peroxo-polytungstic acids are formed in which chelating $[O_2]^{2-}$ ligands prevent the formation of an oxide network. Such solutions are specially convenient for the deposition of optically transparent thin films. Mixed oxides WO_3-MoO_3 are obtained when condensation is performed in the presence of Mo^{6+} cations.

This paper shows how the condensation of tungstic acid can be chemically controlled and describes the electrochemical properties of the films deposited from such solutions.

1. Introduction

Amorphous and crystalline tungsten oxides WO_3 have been widely studied since the discovery of their electrochromic properties [1]. Thin films reversibly turn to blue upon electrochemical reduction. A mixed valence Li_xWO_3 oxide is formed via the double injection of Li^+ and electrons. Tungsten ions then formally exhibit both W^{6+} and W^{5+} oxidation states and the blue coloration arises from an optically activated hopping process between both valence states [2].

Amorphous WO_3 thin films are currently used for electrochromic applications. They exhibit fast switching time and good reversibility. They can be made by a variety of techniques such as electron beam deposition, sputtering or vapor deposition [2]. They have also been deposited via the sol-gel route from tungsten ethoxide $W(OEt)_6$ or chloroalkoxides $WOCl_x(OEt)_{4-x}$ [3-5]. However, tungsten alkoxides are very sensitive to moisture and aqueous precursors would be more convenient for large scale production.

Colloidal solutions of tungstic acids have been prepared via the acidification of aqueous tungstate solutions. Their electrochromic properties are rather good but solutions are not stable and a $WO_3 \cdot 2H_2O$ precipitate is formed after few hours [6]. This hydrated oxide is not suitable for the deposition of optically transparent thin films. The condensation of tungstic acid has then to be controlled in order to avoid precipitation.

This paper presents two different ways to overcome this drawback. The first one is to synthesize mixed WO_3-MoO_3 oxides. The condensation of molybdic acid H_2MoO_4 remains limited to solute species and precipitation is not observed even after few months. The other one is to dissolve tungstic acid H_2WO_4 into an aqueous solution of H_2O_2. Peroxo ions $[O_2]^{2-}$ behave as complexing reagents and prevent further condensation giving stable solutions of peroxo-poly-tungstic acid [7].

2. Synthesis and Properties of Hydrated Tungsten Oxide

2.1. Synthesis of Polyoxotungstic Acid. Colloidal tungsten oxide is formed via the acidification of a tungstate solution $Na_2WO_4{\cdot}2H_2O$ through a proton exchange resin. A transparent solution of tungstic acid H_2WO_4 is first obtained. Condensation then leads to opalescent colloidal solutions or gels. The precipitation of a crystalline hydrate $WO_3{\cdot}2H_2O$ occurs after few hours when the gel is left in its mother solution.

Thin films can be deposited by spraying a fresh colloidal solution onto a substrate. An amorphous hydrous oxide $WO_3{\cdot}nH_2O$ ($n \approx 1.6$) is formed when the coating is dried under ambient conditions. The amount of water in the film depends on the drying conditions. Most water molecules can be reversibly removed under vacuum or upon heating at 120°C leading to $WO_3{\cdot}0.6H_2O$. Beyond that temperature the dehydration process is no more reversible. Hydration occurs when the film is left in a humid atmosphere giving the well known crystalline hydrate $WO_3{\cdot}2H_2O$ [8].

2.2. Electrochromic Properties of Hydrated Tungsten Oxides. The electrochromic properties of the films deposited from colloidal solutions of tungstic acid strongly depend on their hydration state. Faster response times and shorter lifetimes are observed when the water content increases. Cyclic voltammograms were recorded with a classical three-electrodes potentiostatic cell using a platinum grid as counter electrode, $Ag/AgClO_4$ (10^{-2}M) as reference and $LiClO_4$/propylene carbonate as electrolyte. Experiments were performed in the range +1V, -2V with thin films deposited onto a glass electrode covered with a $SnO_2{:}F$ coating. A He-Ne laser beam (λ=632.8nm) goes through the electrochemical cell allowing in situ optical absorption measurements to be done while cyclic voltammograms are recorded. The number of charges Q exchanged during these experiments can be deduced from the surface of cyclic voltammetric curves and the reversibility of the process can be expressed by the ratio Q_{red}/Q_{ox}.

Continuous curves are observed with the hydrated xerogels $WO_3{\cdot}nH_2O$ (Fig. 1a). They are typical of amorphous compounds in which Li^+ insertion occurs at random. As expected, several peaks can be seen on the cyclic voltammogram of the crystalline layered $WO_3{\cdot}2H_2O$ compound (Fig. 1b) [8]. The electrochromic properties of the less hydrated $WO_3{\cdot}0.6H_2O$ films are poor. The amount of inserted Li^+ ions remains small (Q_{red}=7 mC/cm^2) and the process is poorly reversible (Q_{ox}/Q_{red}=0.5). Much better results are obtained when the amount of water increases. More Li^+ ions are inserted (Q_{red}=18 mC/cm^2 for amorphous $WO_3{\cdot}1.6H_2O$ and 15 mC/cm^2 for crystalline $WO_3{\cdot}2H_2O$) and the reversibility reaches 95% after the first cycle.

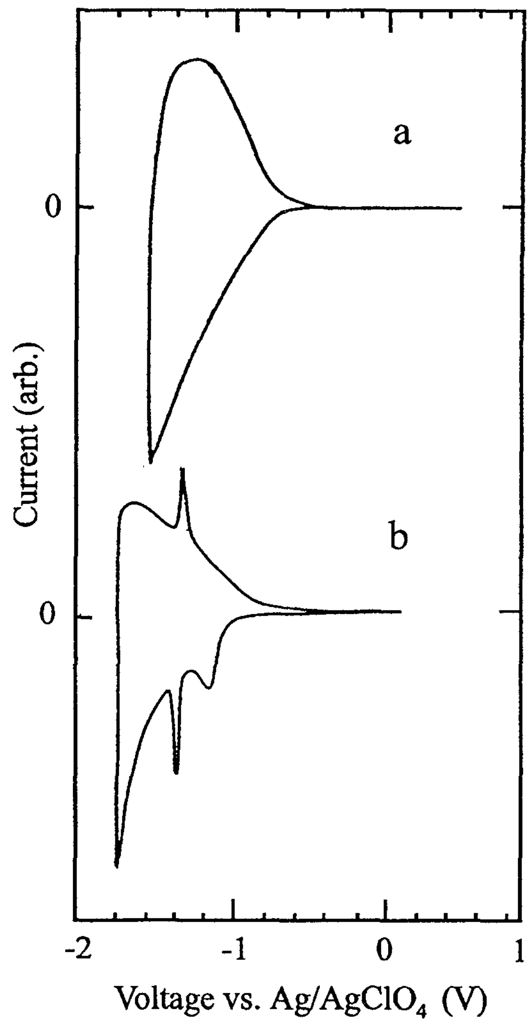


Fig. 1. Cyclic voltammograms of $WO_3{\cdot}nH_2O$ thin films (a) amorphous $WO_3{\cdot}1.6H_2O$, (b) crystalline $WO_3{\cdot}2H_2O$.

3. Mixed WO_3-MoO_3 Oxides

3.1. Synthesis of Stable Colloidal Solutions. Colloidal solutions of mixed WO_3-MoO_3 oxides have been prepared from aqueous solutions of sodium tungstate and molybdate. Such as above, the mixed solution is passed through a proton exchange resin. A transparent yellow solution is obtained after acidification that remain more or less stable

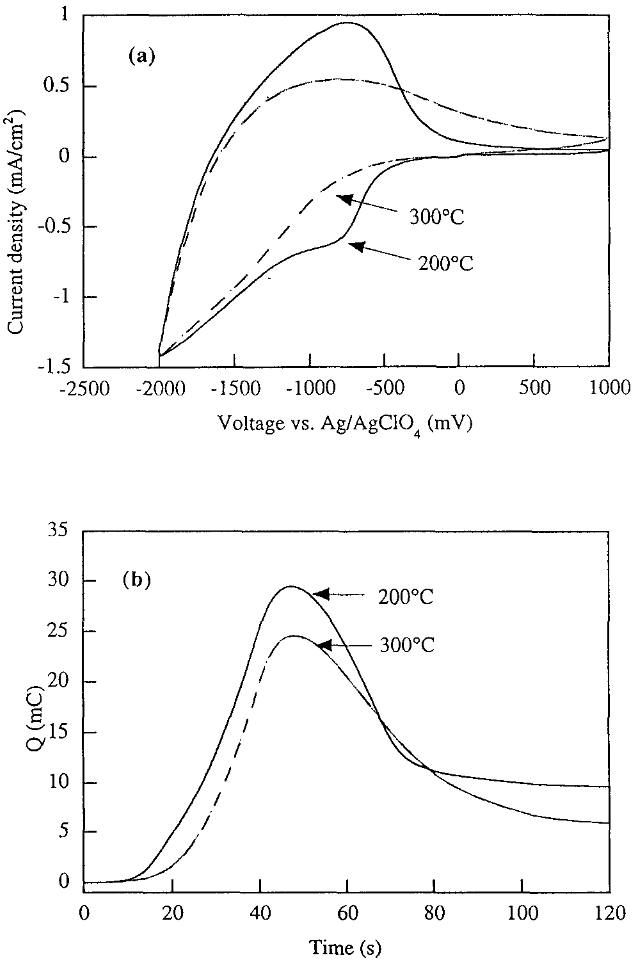


Fig. 2. Electrochemical insertion of Li$^+$ in WO$_3$-MoO$_3$ (75-25) films heated at 200 °C and 300 °C (first cycle). (a) cyclic voltammetry curve, (b) inserted charge.

depending on the amount of Mo. Solutions containing a molar ratio Mo/W$\geq$20/80 remain stable for more than a week. Below this value precipitation occurs within few days. Light scattering experiments show that they are made of colloidal particles about 1-2 nm in diameter.

Optically transparent thin films can be dip-coated from the solution (molar ratio Mo/W=25/75). However as-deposited films are amorphous and soluble in propylene carbonate. They have to be heat treated between 200 and 300°C. The films remain amorphous but are no longer soluble and can be used in an electrochromic cell in the presence of a liquid electrolyte (LiClO$_4$ in propylene carbonate).

3.2. Electrochromic Properties of Thin Films. Cyclic voltammetry experiments have been performed on films deposited from fresh solutions and heated at 200 or 300 °C (Fig. 2a). During the first cycle Li$^+$ insertion is more reversible for films heated at 300 °C (Fig. 2b).These differences decrease when the number of cycles increases and after 100 cycles the electrochemical properties of both films are quite similar (Fig. 3). The optical absorption of the film heated at 300 °C remains anyway slightly better (Fig. 3c).

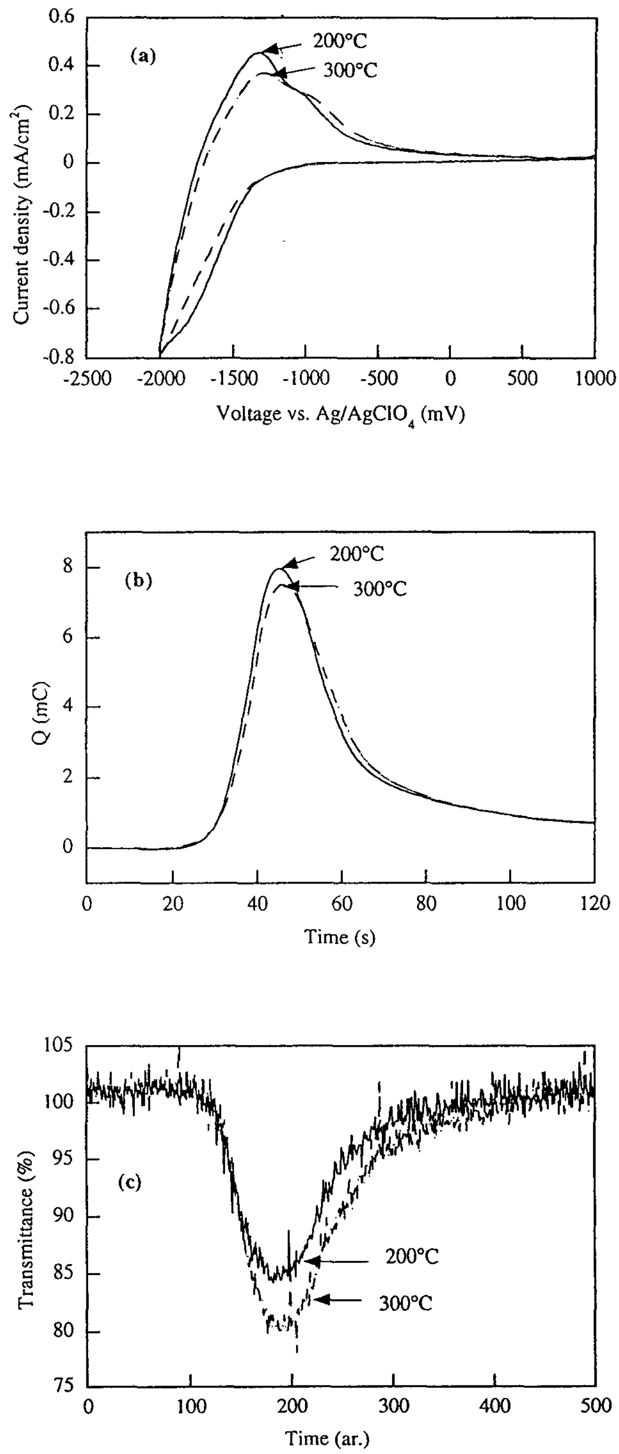


Fig. 3. Electrochemical insertion of Li$^+$ in WO$_3$-MoO$_3$ (75-25) films after 100 cycles. (a) cyclic voltammetry curve, (b) inserted charge, (c) optical transmittance.

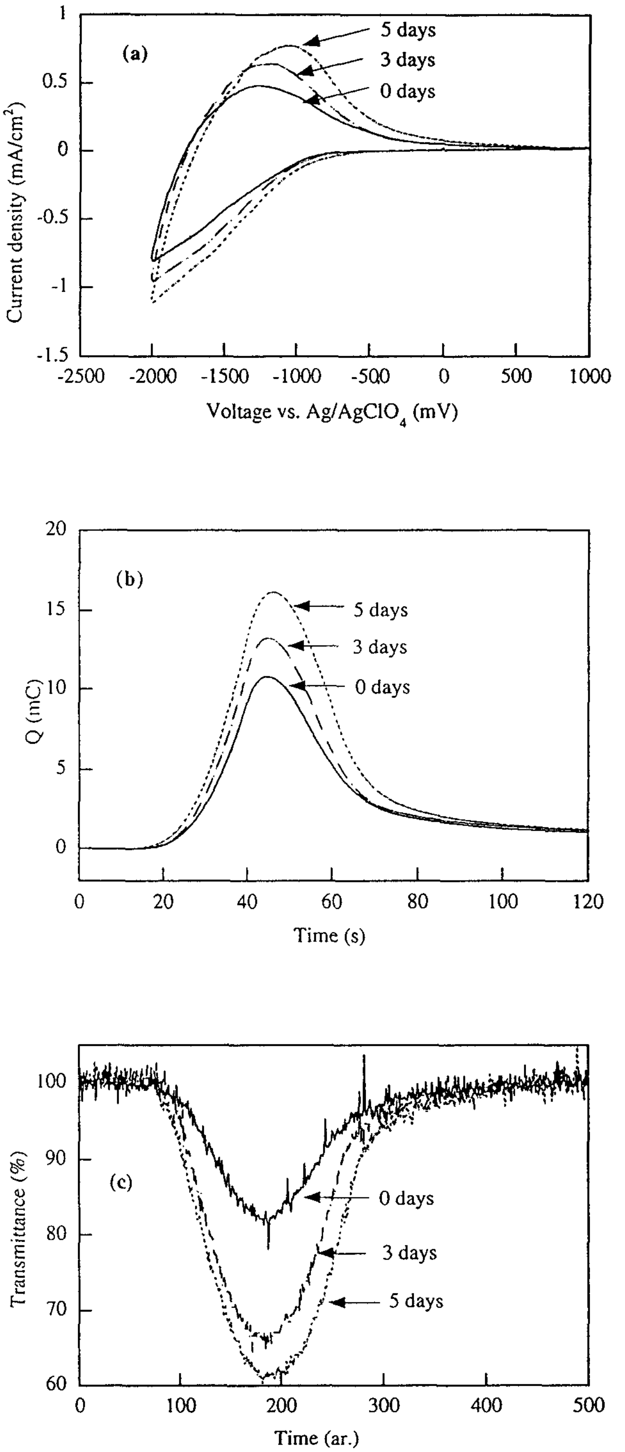


Fig. 4. Electrochemical insertion of Li^+ in WO_3-MoO_3 (75-25) films after aging (30th cycle). (a) cyclic voltammetry curve, (b) inserted charge, (c) optical transmittance

Figure 4 shows that the electrochromic properties of the films heated at 300 °C improve when the solution is aged for few days before deposition. The injected charge for instance increases from 10 to 17 mC/cm^2 (Fig. 4b) after 5 days and the optical transmittance decreases from 82 % down to 62 % of the initial transmittance of the bleached state (Fig. 4c).

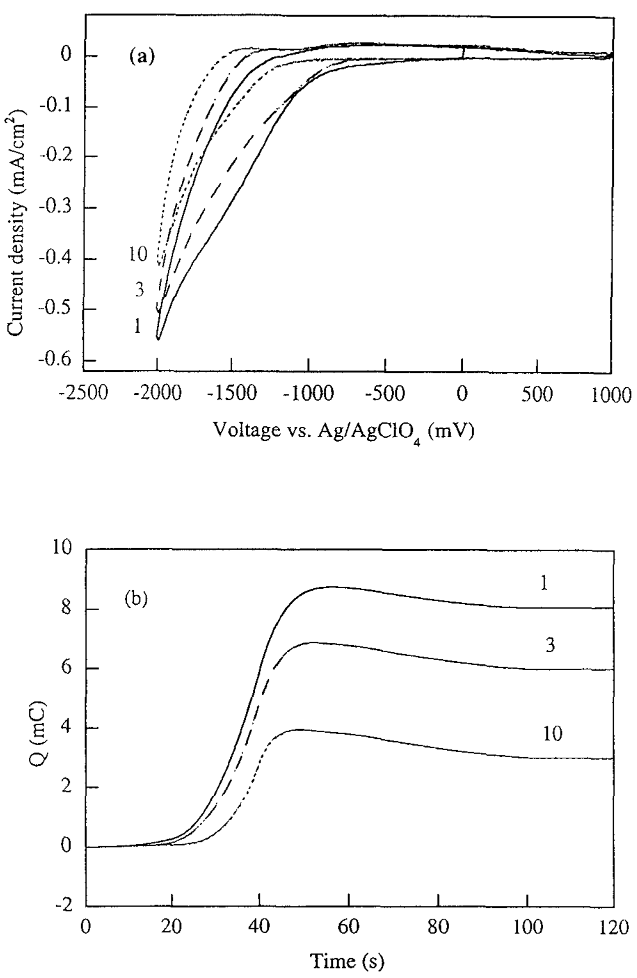


Fig. 5. Electrochemical insertion of Li^+ in crystalline "$WO_3{\cdot}H_2O_2{\cdot}H_2O$" films as a function of the number of cycles. (a) Cyclic voltammetry curves, (b) inserted charge

4. Peroxopolytungstic Acid

4.1. Synthesis of Peroxopolytungstic Acid. Peroxopolytungstic acid was obtained via the dissolution of commercial tungstic acid H_2WO_4 in an aqueous solution of hydrogen peroxide (30 % H_2O_2) [9]. Dissolution is performed at 60 °C for few hours under continuous stirring giving a pale yellow acid solution about 0.4M in tungsten (pH≈1). These solutions are very stable as long as H_2O_2 remains in excess. They can be kept for months at room temperature without precipitation. Dipping a platinum net into the solution leads to the decomposition of H_2O_2 and the rapid formation of a precipitate.

Thin films, about 0.5 µm thick, are deposited by dip-coating a glass substrate into the H_2WO_4-H_2O_2 solution.

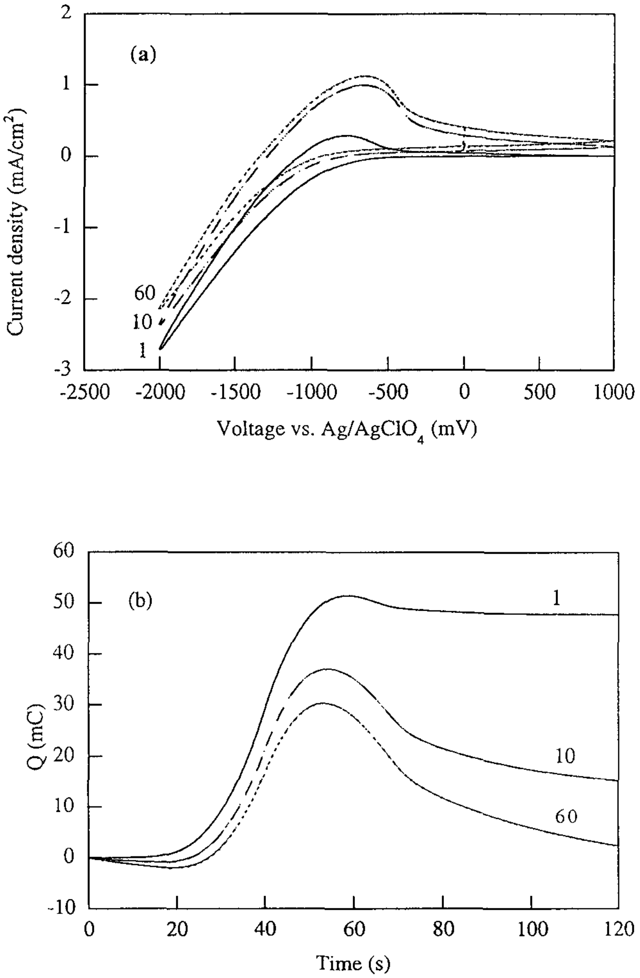


Fig. 6. Electrochemical insertion of Li^+ in amorphous WO_3 films (heated at 260 °C) prepared from peroxopolytungstic acid films as a function of the number of cycles. (a) cyclic voltammetry curves, (b) inserted charge

The slow evaporation of the solvent at room temperature leads to the formation of a crystalline film corresponding to the "$WO_3 \cdot H_2O_2 \cdot H_2O$" phase described by Kudo et al. [10]. Water is removed and peroxo groups are decomposed upon heating giving an amorphous oxide at 230 °C and then the usual monoclinic oxide WO_3 beyond 400 °C.

4.2. Electrochromic Properties of Peroxopolytungstic Acid. The cyclic voltammetry curves of thin films heated at different temperatures have been recorded in order to study the electrochemical properties of the different phases formed via the deposition of peroxopolytungstic acid.

The electrochromic properties of the crystalline peroxo phase "$WO_3 \cdot H_2O_2 \cdot H_2O$" are very poor (Fig. 5). Lithium insertion during the first cycle is not reversible (Q_{ox}/Q_{red} = 8 %). It improves slightly upon cycling but only 24% of the initial capacity is recovered after 10 cycles (Fig. 5b).

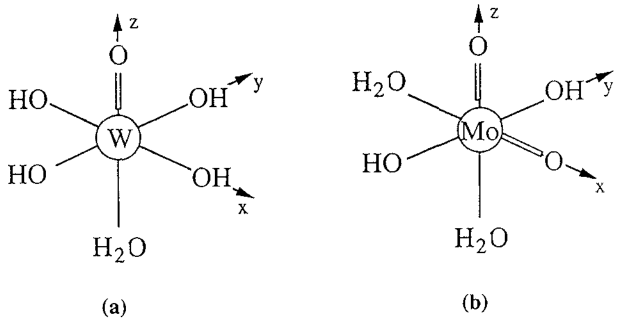
Much better results have been obtained with an amorphous film heated at 260 °C (Fig. 6). The reversibility is not good during the first cycle as only 7% of the injected charge can be removed. However its properties improve significantly upon cycling and the coulombic ratio reaches 92% after 60 cycles (Fig. 6b).

5. Conclusion

This paper shows that electrochromic WO_3 based thin films can be made from different precursor solutions [11].

The tungsten oxide WO_3 is formed via the condensation of the neutral precursor $[WO(OH)_4(OH_2)]^0$ in which one water molecule is bonded along the z axis opposite to the W=O bond while the four OH groups are in the equatorial xy plane (Fig. 7a). Oxolation along equivalent x and y directions leads to the precipitation of a hydrated oxide $WO_3 \cdot 2H_2O$, made of corner sharing $[WO_6]$ octahedra. The water molecules are intercalated between the oxide layers. Oxolation reactions involve four W-OH groups and lead to the fast formation of an oxide network. Intermediate colloidal solutions are not stable toward condensation and precipitation occurs rapidly. Colloidal species have then to be stabilized by preventing the growth of oxide particles.

As for tungstic acid, molybdenum oxide phases are formed via the condensation of the neutral precursors $[MoO_6H_6]^0$. However, the Mo^{6+} ion is smaller and therefore more polarizing than W^{6+}. This leads to the formation of dioxo $[MO_2(OH)_2(OH_2)_2]^0$ precursors in which two Mo=O double bonds are formed in order to decrease the positive charge of the Mo^{6+} cation. The neutral precursor exhibits only two Mo-OH groups instead of four in the case of W^{VI} (Fig. 7b). Condensation reactions via



(a) (b)

Fig. 7. Molecular structure of neutral precursors. (a) for WO_3, $[WO(OH)_4(OH_2)]^0$, (b) for MoO_3, $[MoO_2(OH)_2(OH_2)_2]^0$.

oxolation are therefore limited giving rise to small solute species. Pure molybdic acid solutions remain stable for months without precipitation. Mixed WO_3/MoO_3 precursors exhibit intermediate reactivities and stable solutions can be obtained when enough Mo is added in order to decrease the number of reactive M-OH groups (M = W, Mo).

The precipitation of the hydrated oxide $WO_3 \cdot 2H_2O$ can also be prevented by adding hydrogen peroxide to the solution of precursor. The dissolution of tungstic acid leads to the formation of peroxo-polytungstic acid species such as $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ in which W^{VI} ions are complexed by chelating $[O_2]^{2-}$ ligands [12].

6. Acknowledgments

Authors would like to acknowledge Guillermo Guzman, Hélène Lecacheux and Roger Morineau for their contribution to this work. S. Castro-Garcia acknowledges Caixa Galicia the financial support.

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Paper presented at the 4th Euroconference on Solid State Ionics, Renvyle, Galway, Ireland, Sept. 13-19, 1997

Manuscript rec. Sept. 17, 1997; acc. Oct. 10, 1997